

5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Tin is a naturally-occurring element found in environmental media in inorganic and organic compounds. Tin may be released to the environment from natural and anthropogenic sources. The most significant releases of tin are from burning of fossil fuels and industrial production and use of tin. Tin compounds are generally only sparingly soluble in water and are likely to partition to soils and sediments. Photodegradation and biodegradation of organotins may occur at relatively slow rates. Organotin compounds may be significantly bioconcentrated by aquatic organisms.

Ambient environmental levels of tin are generally quite low, except in the vicinity of pollution sources. Humans may be exposed to tin by inhalation, ingestion, or dermal absorption. However, human exposure to tin is primarily by ingestion of food, especially canned food products.

Occupational exposure to tin may be significant in some industrial environments.

The EPA has identified 1,300 NPL sites. Tin has been found at 11 of the 1,177 evaluated sites. As more sites are evaluated by the EPA, the number may change (View 1989). The frequency of these sites within the United States can be seen in Figure 5-1.

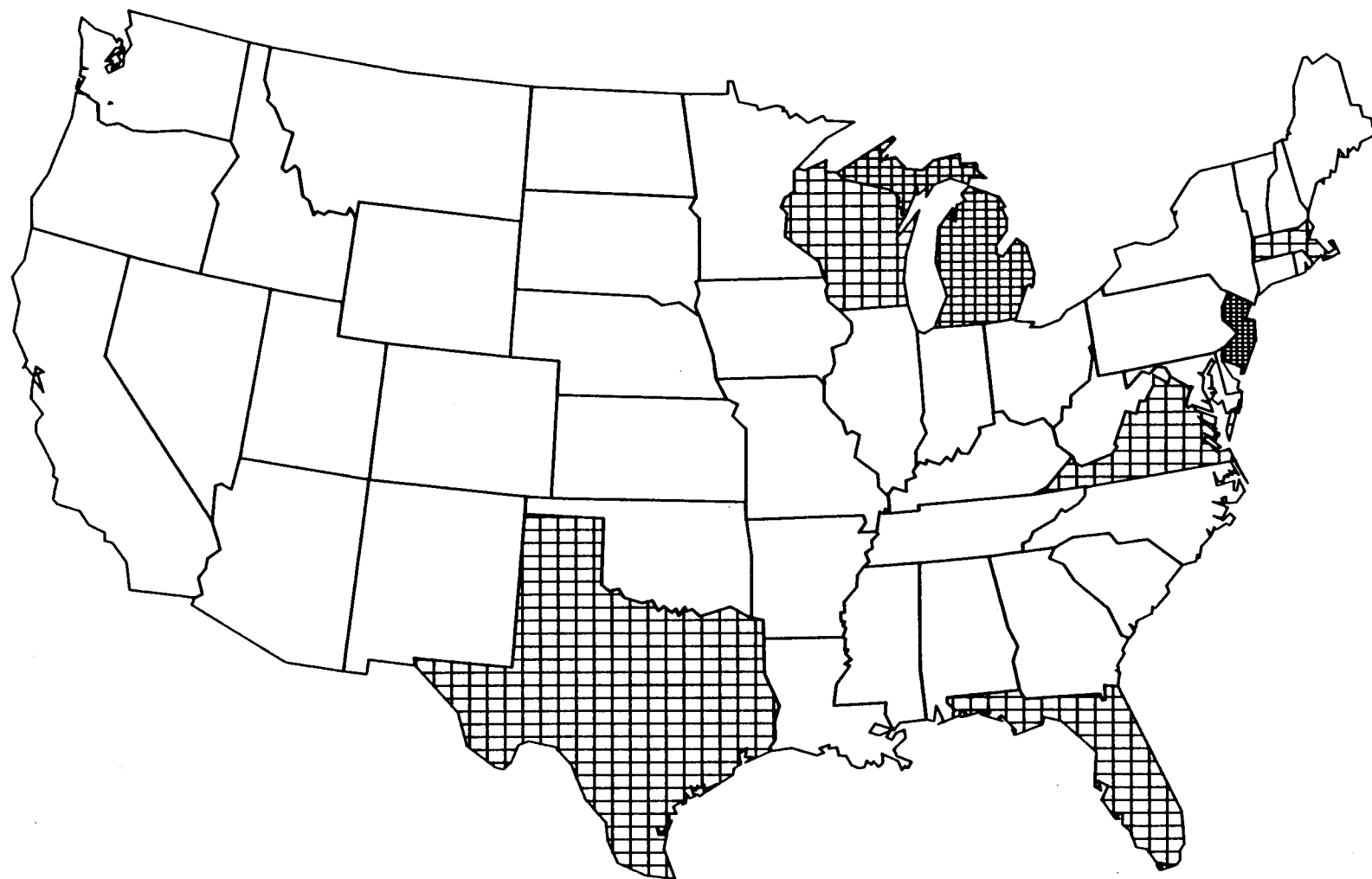
5.2 RELEASES TO THE ENVIRONMENT

Releases of tin to environmental media may occur from the production and use of tin and tin compounds. However, neither tin nor any tin compounds are listed on the SARA Section 313 toxic chemical list and, therefore, are not included in the Toxics Release Inventory (TRI).

5.2.1 Air

Tin may be released to the atmosphere from both natural and anthropogenic sources. Tin is a component of many soils and inorganic tin compounds may be released in dusts from wind storms, roads, and agricultural activities. Gases, dusts, and fumes containing tin may be released from smelting and refining processes, other industrial uses of tin and burning of fossil fuels (WHO 1980). Davison et al. (1974) reported the tin content of airborne fly ash from coal-burning power plants ranged from 7 to 19 $\mu\text{g/g}$. No other quantitative data on tin releases to air in the United States were located, but worldwide emissions of tin to the atmosphere from coal and oil combustion, refuse incineration, and copper/nickel production facilities were estimated at 1,470-10,810 metric tons in 1983 (Nriagu and Pacyna 1988).

FIGURE 5-1. FREQUENCY OF NPL SITES WITH TIN CONTAMINATION *



FREQUENCY  1 SITE  2 SITES  4 SITES

* Derived from View 1989

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5.2.2 Water

Releases of tin to water may occur from industrial facilities smelting, refining, or using tin (WHO 1980). Organotins may be released from agricultural uses or from their use as antifouling coatings on ships, and stabilizers in polyvinyl chloride plastic (EPA 1982a, 1988c; WHO 1980). No quantitative data were located regarding tin releases to water in the United States. However, the Organotin Antifouling Paints Control Act of 1988 restricts United States organotin paint usage on ships to those which do not exceed a release rate of 4 μg organotin/ cm^2/day (EPA 1988c).

Elevated tin levels have been detected in both surface and groundwater at hazardous waste sites. Data from the Contract Laboratory Program (CLP) Statistical Database indicate tin occurred at about 21% of the sites sampled at a geometric mean concentration of about 50 $\mu\text{g}/\text{L}$ (CLPSD 1989). The CLP database includes data from both NPL and non-NPL sites. These values may be underestimates, since monitoring for tin was discontinued before 1986.

5.2.3 Soil

Tin may be released to soil from organotin pesticide usage and landfilling of tin-containing wastes, including used cans and organotin-containing plastics (WHO 1980).

More than 5,000 tons of organotins were released, primarily to landfills, in the United States in 1976 (Laughlin and Linden 1985). Additional releases to soil may occur by disposal of fly ash from coal combustion or land application of sewage sludge.

Tin was detected in soil samples at 36% of 455 hazardous waste sites at a geometric mean concentration of 30 mg/kg (CLPSD 1989). The CLP database includes data from both NPL and non-NPL sites. These values may be underestimates, since monitoring for tin was discontinued before 1986.

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

Tin may be transported in the atmosphere by the release of particulate matter derived from the combustion of fossil fuels and solid wastes. The vapor pressure of elemental tin is negligible (Cooper and Stranks 1966). Tin in aerosol samples that existed in particulate-carbon masses was removed from the atmosphere predominantly by gravitational settling (Byrd and Andreae 1986). The half-life of airborne particles is usually on the order of days, depending on the size of the particle and atmospheric conditions (Nriagu 1979). Removal by washout mechanisms (such as rain) is thought to be unimportant.

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However, there is little information on the potential for organotins to volatilize from water. There was no indication that tributyltin in water partitioned to the air during a 62-day period whereas 20% of the water evaporated (Maguire et al. 1983).

It has been speculated that the vapor pressures of some organotin compounds may be high enough such that they could partition to the atmosphere (Donard and Weber 1988; WHO 1980), but no actual measurements were available. The vapor pressure of one organotin, bis(tributyltin) oxide was estimated to be 8.4×10^{-10} atm and essentially nonvolatile (Maguire et al. 1983). Methyltins were not detected in rain-water samples (Byrd and Andreae 1986).

Tin in ambient waters may exist as divalent cationic (positively charged) ions (Sn^{2+}) or as quadrivalent ions (Sn^{4+}). Stannous tin (Sn^{2+}) dominates in reduced (oxygen-poor) water, and will readily precipitate as a sulfide (SnS) or as a hydroxide ($\text{Sn}(\text{OH})_2$) in alkaline water. Stannic tin (Sn^{4+}) readily hydrolyzes, and can precipitate as a hydroxide (Wedepohl et al. 1978). The solubility product of $\text{Sn}(\text{OH})_4$ has been measured as approximately 10^{-56} g/L at 25°C (Wedepohl et al. 1978).

The solubilities of organotin compounds in water are not well known. At ambient temperatures, their solubilities range from 10 µg/L to about 50 mg/L (Laughlin and Linden 1985; WHO 1980). It has been estimated that the solubility of bis(tributyltin) oxide ranges from 0.7 to 7 mg/L at pH 6 (Maguire et al. 1983).

Tin in water may partition to soils and sediments. Cations such as Sn^{2+} and Sn^{4+} will generally be adsorbed by soils to some extent, which reduces their mobility. Tin is generally regarded as being relatively immobile in the environment (WHO 1980). However, tin may be transported in water if it partitions to suspended sediments (Cooney 1988), but the significance of this mechanism has not been studied in detail.

The adsorption-desorption properties of inorganic tin have not been studied, and little information is available for organotins. Many organotins occur in water as cations, and would be expected to partition to soils and sediments. A partition coefficient of about 2,180 at 20°C was calculated by Maguire et al. (1985) to estimate the adsorption of tributyltin ions (as Bu_3Sn^+) by lake sediments. These investigations also concluded that the half-life of the desorption reaction was about 10 months, indicating that tributyltin can be strongly retained by sediments. Other studies (Cooney 1988; EPA 1988a; Strand 1983) have speculated that organotins may be bound by soil, but no additional information was located.

Tin may partition from water to aquatic organisms. An octanol/water partition coefficient (K_{ow}) describes the partitioning of an organic chemical between octanol and water. Octanol is believed to best imitate the fatty structures in plant and animal tissues (Kenaga and Goring 1980). The K_{ow} of tributyltin at pH 6 was reported as about 1,585 by Maguire et al. (1983). The most accurate K_{ow} for tributyltin in sea water was 5,500 (Laughlin and Linden

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1985) and Tsuda et al. (1986) reported that the K_{OWS} of seven organotin compounds ranged from 9 to 4,571. The magnitude of these values suggest that organotins can partition to fat tissues significantly, depending on the specific compound.

A bioconcentration factor (BCF) relates the concentration of a chemical in plants and animals to the concentration of the chemical in the medium in which they live. It was estimated that the BCFs of inorganic tin were 100, 1,000, and 3,000 for marine and freshwater plants, invertebrates, and fish, respectively (Thompson et al. 1972). Marine algae can bioconcentrate stannic tin by a factor of 1,900 (Seidel et al. 1980). No other experimentally derived BCFs for inorganic tin were located. The BCF of tributyltin was estimated to be 473, but measured BCFs were always higher (Laughlin and Linden 1985). Bioconcentration factors for bis(tributyltin)oxide with marine oysters were measured as 2,300 to 11,400 (Waldock and Thain 1983). A BCF of 30,000 was estimated by Maguire et al. (1984) for the bioconcentration of tributyltin cation Bu_3Sn^+ by freshwater green algae. Seven-day BCFs were derived for seven organotin compounds for muscle, liver, kidney, and vertebra tissue of carp (Tsuda et al. 1986). The BCFs ranged from 12 to 5,012; the highest factors were found for tributyltins. However, these factors were not based on steady-state conditions, and may be low estimates. No information was located on the food chain and biomagnification of inorganic or organic tin.

5.3.2 Transformation and Degradation

5.3.2.1 Air

No information was located on the transformation or degradation of tin compounds in the atmosphere.

5.3.2.2 Water

There is no evidence that the valence of inorganic tin is influenced directly by microbial processes (Cooney 1988). It has been established that inorganic tin can be transformed into organometallic forms by microbial methylation (Hallas et al. 1982). Inorganic tin may also be converted to stannane (H_4Sn) in extremely anaerobic (oxygen-poor) conditions by macroalgae (Donard and Weber 1988).

It has been reported that low concentrations of tributyltin fluoride were readily transformed to tributyltin chloride in sea water (Strand 1983). Tributyltin has been shown to undergo slow photolysis (Maguire et al. 1983). The half-life of the photolysis reaction was estimated to be greater than 89 days. The direct photolysis of tributyltin in water initiates a sequential removal of the butyl groups, leading to inorganic tin as a residual. The reaction was much faster in the presence of fulvic acid (a major component of soil organic matter).

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The biodegradation of organotins in water may or may not be a slow process. Under laboratory conditions, Maguire and Tkacz (1985) estimated that the half-life of tributyltin in water was about 35 weeks in the dark, and like photolytic reactions, involved debutylation. They concluded that tributyltin was a fairly persistent chemical in the environment. The overall half-life of tributyltin (photolysis and biodegradation) in water was estimated to be on the order of months in Canadian lakes. However, the half-life of tributyltin in river waters in Georgia was estimated to be between 3 and 13 days (Lee et al. 1989). The degradation of the chemical was attributed to microalgae whereas direct photolysis did not appear to be important. The half-life of tributyltin via degradation by algae in water/sediment mixtures was estimated to be about 25 days (Maguire et al. 1984), but the concentration of algae used in the experiment was much greater than that expected in lakes (Maguire and Tkacz 1985).

5.3.2.3 Soil

Organotins may also be slowly biodegraded when in contact with soils and sediments. Alkane-utilizing bacteria were isolated from soil that could degrade the tributyl forms to di- and monobutyltin, but further breakdown was not observed.

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1 Air

Tin is detected in air infrequently at low concentrations, except in the vicinity of industrial sources. Air concentrations in United States cities ranged from below the detection limit to $0.8 \mu\text{g}/\text{m}^3$ in several studies (WHO 1980). Average concentrations are generally $<0.1 \mu\text{g}/\text{m}^3$, with the higher concentrations near some industrial facilities (EPA 1982a; WHO 1980). In some studies, tin was not detected in 40% to more than 50% of samples (WHO 1980). Atmospheric tin is associated with particulate matter and peak concentrations were found on smaller respirable particles (1 to $3 \mu\text{m}$) (WHO 1980).

5.4.2 Water

Tin occurs in trace amounts in natural waters. However, it is seldom measured and only infrequently detected, since concentrations are often below the detection limit (NAS 1977; WHO 1980). In surface waters, tin was detected in only three of 59 samples from 15 United States and Canadian rivers at concentrations ranging from 1.3 to $2.1 \mu\text{g}/\text{L}$, and not detected in 119 samples from 28 United States rivers. A mean tin concentration of $0.038 \mu\text{g}/\text{L}$ was reported for surface water in Maine (NAS 1977; WHO 1980). Organotin concentrations in the Detroit and St. Clair Rivers ranged from not detected to $0.11 \mu\text{g}/\text{L}$ (Maguire et al. 1985).

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Tin concentrations in public water supplies reportedly ranged from 1.1 to 2.2 µg/L in 42 United States cities and from 0.8 to 30 µg/L in 32 of 175 water supplies in Arizona (NAS 1977; WHO 1980). Tin is present in seawater at about 0.2-3 µg/L (NAS 1977; WHO 1980).

Tributyltin has been monitored in harbor areas due to concern about release of this compound to water from antifouling paints and its toxicity to aquatic life. Concentrations reported ranged from not detected to 0.8 µg/L (EPA 1988c). Reported total organotin concentrations in surface water ranged from 0 to 900 mg/L (EPA 1982a).

5.4.3 Soil

Tin concentrations have been reported in sewage sludge from 23 United States cities ranging from 11 to 1,300 mg/kg (Mumma et al. 1984). Organotin concentrations in sediments from the Detroit and St. Clair Rivers ranged from not detected to 0.036 mg/kg (Maguire et al. 1985).

Soil concentrations of tin generally range up to 200 mg/kg, but in areas of high tin deposits levels of 1,000 mg/kg may occur (Schafer and Fembert 1984; WHO 1980). Mean background soil concentration in the U.S. is 0.89 mg tin/kg (Eckel and Langley 1988).

5.4.4 Other Environmental Media

Most natural foods contain small amounts of tin but canned foods may have significant tin levels (NAS 1977; WHO 1980). Tin concentrations in fresh meats, cereals, and vegetables reportedly range from 0.1 to 1.0 mg tin/kg (Schafer and Femfert 1984). However, concentrations of tin ranging from 1.8 to 500 mg/kg have been reported in canned foods (Schafer and Femfert 1984; Sherlock 1987), with usual values below 100 mg/kg (NAS 1977). Foods from all-lacquered cans usually had tin concentrations below 25 mg/kg (WHO 1980). Current data from the Can Manufacturers Institute (CMI 1988) indicate that more than 90% of tin-lined cans used for food today are lacquered. Only light colored fruit and fruit juices are packed in unlacquered cans, since tin helps maintain the color of the fruit.

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Human exposure to tin may occur by inhalation, ingestion, or dermal contact. However, exposure of the general population occurs primarily by ingestion of food (NAS 1977; WHO 1980). Estimates of daily dietary tin intake range from 1 mg for diets consisting mainly of fresh meats, vegetables, and cereals, to 38 mg from diets including a high proportion of canned foods (Schafer and Femfert 1984; WHO 1980). The average daily tin intake of an adult in the United States was estimated at 4.003 mg; 4 mg from food, 0.003 mg from air, and with undetectable levels contributed by drinking water (EPA 1987a; WHO 1980). Other estimates of human daily intake range from 0.2 to 17 mg (Klaassen et al. 1986; Krigman and Silverman 1984). Tin was detected in

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human adipose tissue samples during the 1982 National Human Adipose Tissue Survey at concentrations ranging from 8.7 to 15 µg/g (Stanley 1986).

Occupational exposures to tin may be substantial. Inhalation or dermal exposure to triphenyltin leachate, used in fungicides and insecticides, may occur during both manufacturing and application (NAS 1977; WHO 1980). Workers in the numerous industries producing or using inorganic tin or organotin compounds (Section 4.3) may also be exposed. The National Institute for Occupational Safety and Health estimated that 730,000 workers in the United States were potentially exposed to tin in the workplace in 1980 (NOES 1989). The NOES database does not contain information on the frequency, concentration, or duration of exposure to workers to tin or any of its compounds. These surveys provide only estimates of number of workers potentially exposed to chemicals in the workplace.

5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Potentially high inhalation exposures to tin and its compounds may occur in the workplace or in agricultural uses of tin compounds.

Individuals who eat canned foods as a major portion of their diets or who store food, especially acidic foods, in opened cans may have potentially above-average exposure to inorganic tin by ingestion. In addition, those populations living near hazardous waste sites where high levels of tin have been detected may be exposed to higher than background levels of tin.

5.7 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of inorganic tin or organotin compounds is available. Where adequate information is not available, ATSDR, in conjunction with the NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of inorganic tin or organotin compounds.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that, if met, would reduce or eliminate the uncertainties of human health assessment. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

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5.7.1 Data Needs

Physical and Chemical Properties. The chemical behavior of most of the common organotin compounds in environmentally-relevant media are not well known. There is a need to measure the solubility and vapor pressure of the more important organotin compounds in order to provide a more reliable basis for predicting their fate in the environment.

Production, Import/Export, Use, and Disposal. Production volumes and uses of tin and tin compounds are well-documented (HSDB 1989; U.S. Bureau of Mines 1989; WHO 1980). However, data on releases, disposal practices, and possible environmental contamination from uses of tin and its compounds are limited. Since tin is not on the TRI and is not listed as an EPA hazardous waste constituent, current data are not available on industrial releases or disposal practices. Information on releases or disposal practices, and current quantitative data on leaching of inorganic and organic forms of tin into foods from tin-lined cans and polyvinyl chloride packaging materials would be useful in assessing potential human exposure to tin compounds.

Environmental Fate. Few data are available on the partitioning, transport, or transformation of tin compounds. From the information available it appears likely that both inorganic and organotin will partition to soils and sediments, but will not volatilize from water (Cooney 1988; Maguire et al. 1983, 1985; WHO 1980). Little is known about the degradation or transformation of tin compounds in air, water, or soil. The information that is available is at best semi-quantitative and geographically-specific (Lee et al. 1989; Maguire et al. 1983, 1984; Maguire and Tkacz 1985). Research on physical and biological processes in water and at sediment-water interfaces would be particularly helpful to more accurately predict the fate of tin compounds released to the environment.

Bioavailability from Environmental Media. Inorganic tin is not well absorbed after inhalation, oral, and dermal exposure. Organotins are somewhat better absorbed by both the inhalation and oral routes, but dermal absorption is not considered important (Hiles 1974; Mori et al. 1984). The daily intakes of tin from air, food, and water are small (WHO 1980). Studies on the availability of tin compounds from soils would be useful in assessing human exposure from ingesting contaminated soils. Further study of human intake of organotin compounds from food and water would also be useful.

Food Chain Bioaccumulation. It has been established that organotins can be bioconcentrated by aquatic organisms in marine environments (Laughlin and Linden 1985; Waldock and Thain 1983). Similar information for terrestrial ecosystems would be useful. Inorganic tin compounds may also be bioconcentrated but data are limited (Seidel et al. 1980; Thompson et al. 1972). There is no information available on the potential transfer of inorganic tin or organotin compounds from lower trophic levels to higher levels. This information would be useful because studies have shown that organotin can be bioconcentrated significantly. However, bioconcentration properties of individual organotin compounds would vary.

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Exposure Levels in Environmental Media. Current data on tin levels in air, water, and food are limited (EPA 1982a, 1988c; NAS 1977; WHO 1980). Additional information on inorganic and organotin concentrations in all media, especially air, water, and soil at hazardous waste sites, determined by the most sensitive analytical methods, would be useful in evaluating human exposure to tin.

Several estimates concerning the human daily intake of tin have been reported (EPA 1987; Klaassen et al. 1986; Krigman and Silverman 1984; WHO 1980). However, these estimates are not based on recent monitoring data and need to be revised in accordance with current data. Since canned food is a primary source of tin exposure, data on current levels of tin in canned foods and revised estimates of daily intake would help to better evaluate human exposure to tin.

Exposure Levels in Humans. Tin has been detected in human adipose tissue (Stanley 1986), but the data are not current. No data were available on biological monitoring for tin in other tissues. Biological monitoring data, especially for populations near hazardous waste sites, would help to assess human exposure to tin.

Exposure Registries. No exposure registries for tin were located. This compound is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. The compound will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to the exposure to this compound.

5.7.2 On-going Studies

No on-going studies on the fate, transport, or exposure potential of tin were located.